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A SIMPLE ROTATING MOLECULAR STILL

A SIMPLE rotating molecular still, designed at the Bureau, makes possible the separation and purification of high-boiling-point materials by a distillation technique.¹ Operating at low temperatures, the molecular still separates these materials rapidly and efficiently, without exposing them to severe thermal decomposition. The rotating molecular still should be especially useful in petroleum research, where various distillation techniques are applied in studying byproducts, and in biochemical and pharmaceutical work as a purification technique.

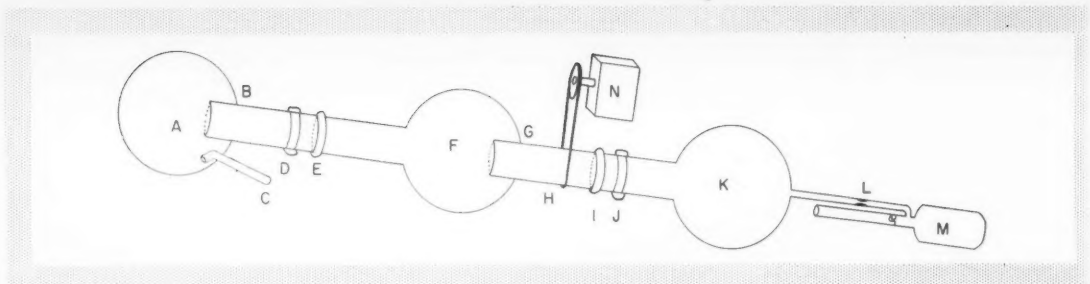
Generally, the rotating evaporators and molecular stills which have been developed in recent years have some disadvantages because of their complex construction. The rotating evaporators, when used as molecular stills, are unsatisfactory in that the system either cannot be evacuated to the required low pressure, or, if lubricated joints are used, the lubricant may contaminate the sample. Also, this type of apparatus is not readily adaptable to multiple stages for distillation. Molecular stills that make use of mobile films operate with an enclosed system, but are quite complex and more expensive than the rotating evaporators. The simplified molecular still, however, can be readily constructed and easily operated. In addition, this apparatus separates materials more rapidly and efficiently than the batch (pot)-type and the falling-film type of molecular still used at the Bureau.

The essential features of the rotating molecular still, designed by G. S. Ross and L. J. Frolen, include two or more 500-ml glass bulbs connected in series, one or more glass ampoules, an infrared lamp, a Dewar containing a refrigerant, and a motor for turning the apparatus. When in operation, the axis of the apparatus is inclined about 10 deg from horizontal. The glass bulb at the high end serves as the container for the sample, and the remaining bulbs act as collectors of the distillate. The glass ampoules in which the distillation fractions are bottled are attached at the lower end of the apparatus.

As the molecular still rotates at 1–2 rpm, the test sample continuously forms a thin surface film on the wall of the container. The infrared lamp heats the film, causing molecules to evaporate from the film's surface. This technique has an advantage in that the bulk of the test sample remains cool, thereby limiting thermal decomposition. Under normal operation the sample is only a few degrees above room temperature.

Gradually the vapor flows toward the adjacent collecting bulb, where it is condensed. The low temperatures are produced in a wide-mouth Dewar flask containing liquid nitrogen or a slurry of solid carbon dioxide in carbon tetrachloride and chloroform. The Dewar flask is placed directly under the collecting bulb.

Repeated distillations can be performed in the same manner by shifting the infrared lamp and the Dewar



Above: In operation the apparatus is inclined about 10 degrees from the horizontal. A, F, K, 500-ml bulbs; B, G, rings; C, entrance tube; D, J, band clamps used as bearings; E, I, alining protrusions; H, rubber O-ring; L, sealing construction; M, ampoule; and N, motor.

Right: Simplified rotating molecular still designed at the Bureau to separate chemicals that have high-boiling points. Besides providing simplicity of design and ease of operation, the apparatus separates these materials more rapidly and efficiently than conventional methods employing molecular distillation.

flask to the adjacent bulbs. After the distillate melts, it is drained into a glass ampoule, which is then sealed off and removed.

The rotating molecular still has been used to remove colored impurities and high-molecular-weight oxidation products from such materials as the halogenated or alkylated dimethylanilines and analogous anisoles. Also, high-boiling residues from crude chlorinated ethyl-benzene stocks have been successfully purified with this apparatus.

¹ For further details, see A simple rotating molecular still, by G. S. Ross and L. J. Frolen, *J. Research NBS*, **62** (May 1959) RP2951.



MANDELKERN RECEIVES FLEMMING AWARD

DR. LEO MANDELKERN, of the Polymer Structure Section, has been selected to receive one of the Arthur S. Flemming Awards for 1958. The awards, sponsored by the Washington Junior Chamber of Commerce and the American Security and Trust Company of Washington, are given annually to ten outstanding young men in the Federal service; five each from the fields of Administration and Science.

Dr. Mandelkern was cited for his "outstanding achievements in scientific research as demonstrated

by the contributions he has made to the chemistry and physics of high polymers." The award was presented at a luncheon on February 19, 1959.

Born in New York City in 1922, Dr. Mandelkern graduated from Cornell University in 1942 with a B.A. degree in chemistry. After four years with the Army Air Force in World War II, he returned to Cornell, where he received his Ph. D. in chemistry in 1949. From 1949 to 1952, he was a post-doctoral fellow at Cornell, performing basic research in the physical chemistry of high polymers.

Dr. Mandelkern joined the Bureau in 1952, and since then has been engaged in experimental and theoretical work on the kinetics of crystallization, melting, and glass transition in polymeric materials. He has also participated in a project to develop better methods of measuring the molecular weight of large molecules.

In 1956, Dr. Mandelkern received the U.S. Department of Commerce Silver Medal for Meritorious Service. He is a member of the American Chemical Society, Sigma Xi, and the Cosmos Club of Washington. He has authored, or made major contributions to, over 40 papers in his field.

Manometer for Calibrating High-Altitude Pressure Devices

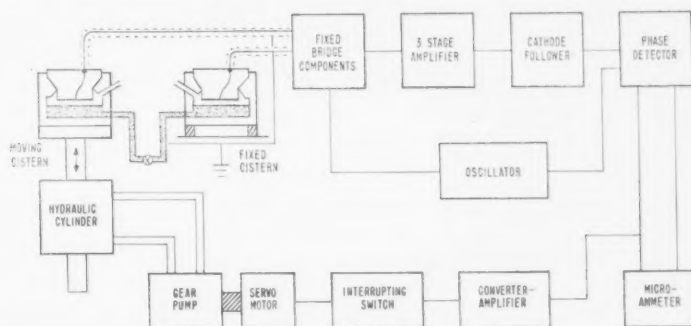
AN experimental 2-in.-range mercury manometer for calibrating pressure-sensing instruments used in present-day military aircraft has been developed by the Bureau under the sponsorship of the Wright Air Development Center. Designed for measuring pressures corresponding to altitudes above 60,000 ft, the manometer employs capacitance measurement as a means of sensing the height of its mercury columns.

The Mechanical Instruments Section undertook the present development to provide an improved calibration standard for calibration of modern flight equipment, such as the air data computer, aiming at an accuracy of 0.0002 in. or better. The resulting manometer achieves this accuracy by incorporating some features of a more complex precision manometer in use at the Bureau.¹

The manometer consists essentially of two mercury cisterns or cups connected by a flexible jointed tube.

Right: Block diagram of the 2-inch range mercury manometer.

Below: Two-inch range mercury manometer for calibrating high-altitude pressure-sensing instruments. Manometer columns are two mercury-filled cisterns. Capacitances formed between cistern covers and column tops are automatically balanced by the raising or lowering of one cistern. Difference between heights of the two cisterns is the pressure in inches of mercury.



One cistern is movable and is connected to a known pressure; the other is stationary and is connected to the pressure to be measured.

The under surfaces of the glass covers of both cisterns are metal coated so that an electrostatic capacitance is formed between the top of each mercury column and the undersides of the covers. These capacitances are balanced by raising or lowering the movable cistern; at balance, the difference in heights between the two corresponds to the difference in height between the mercury columns, and is thus a measure of the unknown pressure.

The positioning of the movable cistern to balance the capacitances is carried out automatically by a supporting piston. The operation is initiated by the voltage generated by imbalance in a bridge circuit containing the capacitances. Upon amplification this signal is fed to a servomotor which drives a pump.

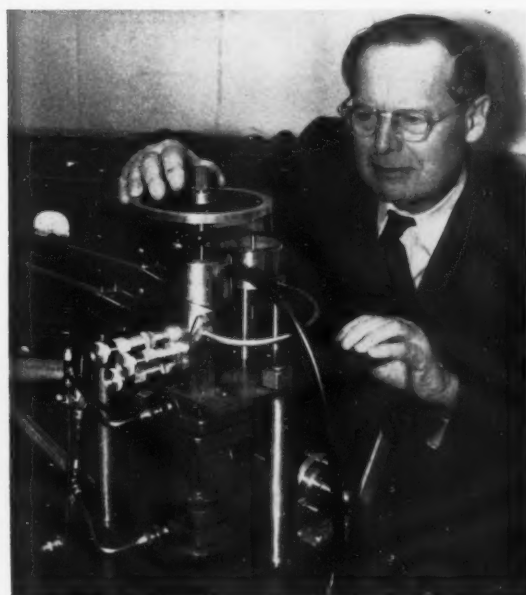
The pump controls the flow of oil to and from the piston, resulting in accurate adjustment of the movable cistern.

Determining the difference in height of the cisterns involves a manual micrometer measurement. Two micrometers, connected by a precision bubble-level, are positioned over the centers of the two covers of the cisterns. As the movable cistern is raised or lowered, the appropriate micrometer is adjusted to keep the bubble-level horizontal. The micrometer reading, showing how far the cistern has been moved, is the pressure difference in inches of mercury.

The manometer may be used to regulate rather than to measure pressure, as essentially the same capacitance-bridge servosystem can be adapted to manipulate a supply valve.

Tests of a preliminary model show that the maximum error in the bridge readings is 0.00011 in. Hg, to which should be added a systematic error in the height reading believed not to exceed 0.00005 in. Hg. The uncertainty is therefore taken as 0.00016 in. Hg.

¹See Precision resistance thermometry and fixed points, by H. F. Stimson, *Temperature: Its measurement and control in science and industry, Vol II*, p. 141 (New York, N.Y., 1955).





VIBRATION OF TELEPHONE



POWER LINES



THE Bureau has been studying the wind-induced vibration of wire conductors under the sponsorship of the Rural Electrification Administration (REA). Object of the study is to reduce vibration so that breakage and wear will be less likely to occur. The work has included a redetermination of the Strouhal number—a basic constant which allows vibrations to be predicted—and an evaluation of the effectiveness of polyethylene sleeves as dampers. This research is part of a continuing program of technical assistance to the REA in which the properties of telephone and power lines are investigated.

A study concentrating on the vibration of conductors became necessary with the introduction of long-span construction to provide economical service in rural areas. High tensions are used in such spans and result in problems in the "wind belt" areas from the Dakotas to Texas and New Mexico. For example, vibration causes conductor wear at the ties and armor rods, and frequently results in breakage, especially in cold weather. It is believed, also, that many of the conductor breaks ascribed to ice and sleet storms actually occur in conductors previously weakened by wind-induced vibrations.

A vertical vibration, characterized by relatively high frequency, low amplitude, and short wavelength, has been observed in wire conductors for many years. This vibration occurs infrequently in the urban systems built with short spans under low tension. However, in rural areas with long-span, high-tension construction, the vibration may occur almost continuously when steady winds prevail. When a wire in such a system

is loaded in tension and fixed at the poles, it has certain natural vibration frequencies. If an alternating force is applied to the wire at a frequency equal to one of these natural vibration frequencies, excessive vibration is apt to result unless some kind of damping has been provided.

Such an alternating force is produced by the distinct vortices in the wake of a wind on the leeward side of the wire. A dimensionless constant, the Strouhal number, relates the frequency of this force to the velocity of the wind and the diameter of the wire. Strouhal number determinations therefore allow vibrations to be predicted and can directly aid in the selection and evaluation of dampers for telephone and power lines.



Typical examples of abrasion and breakage caused by wind-induced vibrations in telephone and power lines.

To determine the Strouhal numbers for several different telephone and power-line conductors, R.R. Bouche and F. J. On of the Bureau's engineering mechanics laboratories, performed a series of wind-tunnel tests. Strouhal number measurements were made on conductors stretched between pulleys across the test section of the wind tunnel. Dead weights produced tension loads of 225 lb, 475 lb, and 925 lb in

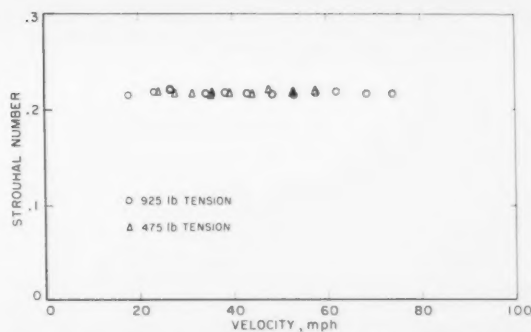
Above: Test set-up for natural-wind vibration test on the roof of one of the buildings at the Bureau. Wires tested are the types most commonly employed as telephone and power lines.

Summary of wind-tunnel tests

Wire type	Diameter	Strouhal number	Wind velocities	Measured frequencies
CSR No. 2 (7 stranded)	.325	.193	6 to 102	78 to 1,067
Copper No. 2 (3 stranded)	.320	.218	18 to 74	210 to 888
CSR No. 4 (7 stranded)	.250	.193	8 to 72	112 to 983
Copper No. 4 (solid)	.204	.198	27 to 95	490 to 1,567
Copperweld 8A (3 stranded)	.199	.184	27 to 64	550 to 1,033
Steel No. 12 (solid polyethylene coated)	.143	.206	11 to 52	275 to 1,300
Steel No. 12 (solid)	.109	.209	10 to 71	333 to 2,367
Copperply No. 080 (solid polyethylene coated)	.112	.211	15 to 43	416 to 1,450
Copperweld No. 080 (solid)	.080	.210	14 to 43	625 to 2,025

the 38½-in. lengths of wire used. To detect the occurrence of resonances in these tensioned wires, a Wheatstone bridge arrangement was made by cementing wire resistance strain gages to both the top and bottom surfaces of the wire along approximately 2½ in. of length near its fixed end. This bridge was connected through an amplification system into an oscillographic recorder.

The velocity of the wind in the tunnel was slowly increased from zero. At the instant the wind, at a known velocity, excited a natural frequency in the wire, the Wheatstone bridge became unbalanced, producing a sinusoidal trace on light-sensitive film in the oscillographic recorder. As the frequency could be determined from the oscillograph record, and the velocity of the wind and the diameter of the wire were known, all the data necessary for calculating the Strouhal number were available.



Strouhal numbers obtained in tests of No. 2 copper wire at tensions of 925 and 475 lb over a wind velocity range of 18 to 74 mph. From the Strouhal number, the frequency of wind-induced vibrations can be determined.

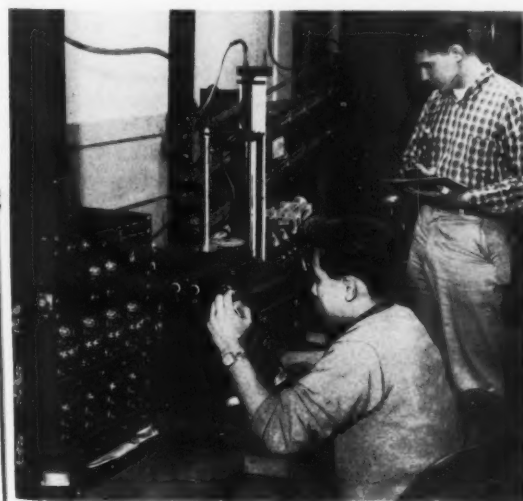
These tests show that the Strouhal number varies somewhat for different types of wire. For most of the conductors tested, the Strouhal number is a little greater than 0.185, the value that has recently been in common use. These determinations establish the relationship between wind velocities and frequencies of the resulting vibrations.

Preliminary studies of vibration by natural winds were carried out on No. 4 solid copper wire. An outdoor test span was located on top of a building at an elevation of approximately 67½ ft above ground. This span was 327 ft long between pulleys and about 10 ft above the roof level—above most obstructions in the vicinity. Here also tension was produced by dead weights.

The wires were found to vibrate in the same manner in the field as in the wind-tunnel tests, regardless of the length of the span. However, it is difficult to determine the Strouhal numbers in the field because of wind-velocity fluctuations. The Strouhal number determined under steady conditions, as in the wind tunnel, should therefore be used to compute either the wind velocity from the frequency measurement or the frequency from wind-velocity measurement.

The field tests also indicate the effectiveness of polyethylene sleeve dampers in eliminating wind-induced vibrations. In carrying out damping comparisons with this outdoor span, a polyethylene sleeve was slipped onto one of two wire lines at 760 lb tension. The half-wave lengths of vibrations were determined by measuring the distance between several nodal points and taking the average. Vibration amplitudes were measured with microscopes at the antinodal point nearest the pulley on the weighted end.

The vibration of an undamped wire was found to be much greater than the vibration of an identical damped wire. In fact, the vibrations in the damped wire were so small that it was difficult to measure them quantitatively. Although these preliminary natural-wind vibration tests indicate the applicability of polyethylene sleeves, further tests are needed to determine optimum sleeve sizes and the economic feasibility of putting these dampers into service for various types of conductors.



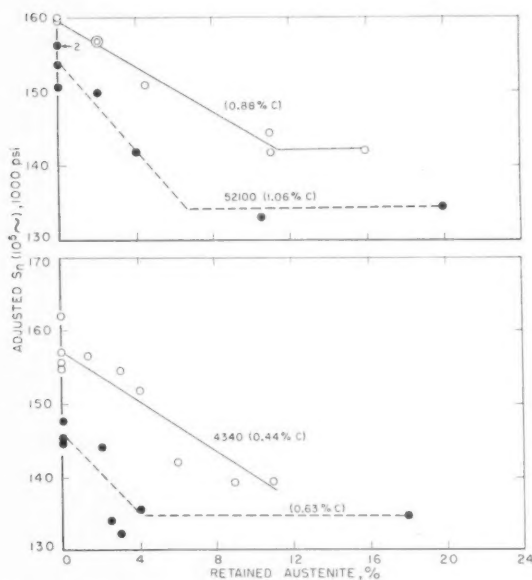
Equipment used to monitor behavior of telephone and power lines in wind-tunnel tests.

Fatigue Properties of High-Strength Steels

IN AN EFFORT to resolve some of the conflicting views concerning the effect of metallurgical structure on fatigue strength of steels, a comprehensive study was recently made at the Bureau. Experiments conducted in cooperation with the University of Maryland showed that retained austenite, in increasing amounts up to 10 percent, lowers fatigue strength.¹ The tests also demonstrated that fatigue stressing transforms retained austenite to untempered martensite, which probably accounts for the deleterious effect. Results of the research are expected to have practical applications in the processing of the high-strength steels used throughout industry.

Although fatigue phenomena have been studied for more than a century, little work has been done on some of the metallurgical aspects of fatigue failure. The present study was undertaken in an attempt to learn how controlled variables—such as carbon content, tempering temperature, cooling method for hardening, and refrigeration—and dependent variables such as retained austenite and hardness are related to fatigue strength. H. E. Frankel and J. A. Bennett of the Bureau staff, and W. A. Pennington of the University's metallurgy department conducted the investigation.

Specimens were made of four low-alloy steels whose carbon contents ranged from 0.44 to 1.06 percent. They were tested on R. R. Moore-type, rotating-beam



Adjusted fatigue strength of the specimens is used to evaluate the effect of retained austenite. These data show that an increase in retained austenite decreases fatigue strength.



Apparatus designed to polish metal specimens. The reduced section is polished parallel to the longitudinal axis of the specimen. (Photo courtesy of IRON AGE.)

fatigue-testing machines that were run at a maximum speed of 8,000 rpm. The machines operated until complete fracture occurred.

Some preliminary experiments indicated that the usual method of preparing fatigue specimens can often mask surface metallurgical effects which may be of prime importance. Consequently, all of the specimens used in the investigation were prepared as follows: Each blank was ground and given a final polish, then copper-plated prior to heat treatment. After heat treatment and stripping of the protective coating, no further polishing was necessary, and the specimens were free from any surface changes induced by mechanical working.

In order to investigate a number of variables with a reasonable number of specimens, an experimental plan was designed using only about one-quarter of all possible combinations of material, quenching procedure, tempering procedure, and tempering temperature. The satisfactory analysis of such an experiment requires that the test results for each condition be expressed by a single number; in this case the stress amplitude which caused failure in 10⁵ cycles was used as a measure of fatigue strength. There was a strong

Chemical composition of materials studied

(Percentage by weight)

Steel	C	Mn	Si	Cr	Ni	Mo
SAE 4340.....	0.44	0.67	0.27	0.77	1.74	0.20
Tool steel #1.....	.63	.60	.21	.70	1.20	.16
Tool steel #2.....	.88	1.51	.28	---	---	.25
SAE 52100.....	1.06	0.34	.19	1.38	---	---

correlation between fatigue strength and hardness; so the data for each steel were adjusted to an average hardness before the effects of other variables were evaluated.

For each steel the adjusted fatigue strengths decreased as the amount of retained austenite (determined by X-ray diffraction analysis) increased. However, for the three higher-carbon steels there appeared to be a limiting value of approximately 10 percent, beyond which no further decrease in strength occurred. Specimens, refrigerated before tempering, were observed to possess greater fatigue strengths than unrefrigerated specimens. These results indicate that refrigeration tends to reduce the amount of retained austenite.

Measurements on tested specimens showed that not only does fatigue stressing transform retained austenite, but that the extent of the transformation depends on the stress amplitude. It is suggested that this

transformation under stress may account for the damaging effect of retained austenite.

At the start of the investigation a basic assumption was made that alloying elements, other than carbon, do not have as much effect on fatigue strength as does the microstructure of the steel. The consistency of the results for the four steels of different alloy content confirmed the validity of this assumption. It was found that as carbon content is increased a higher hardness is necessary for equivalent fatigue strengths. Also, contrary to the results of previous investigators,² no significant difference in fatigue strength was caused by using an interrupted quench.

¹For further technical information, see Fatigue properties of high-strength steels, by H. E. Frankel, J. A. Bennett, and W. A. Pennington, Trans. ASM, Preprint No. 121 (1958).

²Fatigue limit of SAE 1095 after various heat treatments, by Arthur C. Forsyth and Roland P. Carreker, Metal Progr. 54, 683 (1948).

NEW NICKEL OXIDE STANDARD

for spectrographic and chemical analysis

A NEW standard sample of nickel oxide powder is now available from the Bureau. Analyzed and certified for nine minor and trace elements, the standard is intended for checking and calibrating spectrochemical and chemical methods employed in the analysis of high-purity nickel, particularly electronic-grade and electrolytic nickel.

Nickel is available in many forms and, because of its hardness and resistance to corrosion and heat, has many electronic and electrical applications. For instance, nickel is used in support wires and rods, wire mesh for grids, wire for spark plugs, and plates (anodes). The thermionic properties of nickel are also of special interest to the electronics industry. Since these and other properties depend on chemical composition, the new standard should be of value in developing high-purity nickel materials.

The new standard, NBS 673, supplements the nickel oxide standard samples NBS 671 and 672, issued in 1957. All three samples have been prepared by a cooperative program between the Bureau and a task group of Committee F-1 of the American Society for Testing Materials. Similar to the other two, the new standard is designed primarily for application in the spectrographic analysis of nickel and nickel alloys by Tentative Method E 129-57T, *Methods for Emission Spectrochemical Analysis*, American Society for Testing Materials, 1916 Race Street, Philadelphia, Pa., 1957. The three standards are also equally suited for chemical analysis.

The analytical results of nine cooperating laboratories, representing the Bureau and producers and consumers of nickel, are given on a provisional certificate of analyses. The standard has been analyzed and certified for cobalt, copper, iron, magnesium, manganese, silicon, titanium, aluminum, and chromium. The recommended values are given.

Composition of NBS standard sample 673, nickel oxide No. 3

Co	Cu	Fe	Mg	Mn	Si	Ti	Al	Cr
$C_{0.016}^0$	$C_{0.002}^0$	$C_{0.029}^0$	$C_{0.003}^0$	$C_{0.0037}^0$	$C_{0.006}^0$	$C_{0.003}^0$	$C_{0.001}^0$	$C_{0.0003}^0$

The laboratories cooperating in this program are as follows:

Chemical:

National Bureau of Standards, Washington, D.C.;
W. B. Coleman and Company, Philadelphia, Pa.;
Sperry Gyroscope Company, Great Neck, N.Y.;
Superior Tube Company, Norristown, Pa.;
Sylvania Electric Products, Inc., Towanda, Pa.

Spectrochemical:

National Bureau of Standards, Washington, D.C.;
Bell Telephone Laboratories, Murray Hill, N.J.;
W. B. Coleman and Company, Philadelphia, Pa.;
The International Nickel Company, Huntington Works, Huntington, W. Va.;
The International Nickel Company, Research Lab., Bayonne, N.J.;
National Research Corporation, Cambridge, Mass.

The nickel oxide standard is packaged in bottles containing 25 g and is available from the Standard Sample Clerk, National Bureau of Standards, Washington 25, D.C. The fee is \$8.00 per sample. A provisional certificate of analyses accompanying the standard sample lists the analytical results of the cooperating laboratories.

RESEARCH ON FLUOROAROMATIC POLYMERS

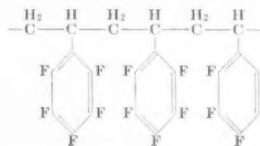
for high-temperature and radiation-resistant materials

TO OBTAIN solid polymeric materials having increased stability, the Bureau has been conducting a research program on the synthesis of fluorocarbons for the Navy Bureau of Aeronautics and the Office of Naval Research. Because most plastic and rubberlike materials cannot withstand temperatures above several hundred degrees, they have only limited application for high-speed aircraft, ordnance equipment, and other types of high-temperature uses. However, it is believed that totally fluorinated aromatic polymers would have greater resistance to high temperatures than any polymeric materials now available. For this reason, the NBS program, under the direction of Dr. Leo A. Wall of the polymer structure laboratory, is being guided toward production of aromatic fluorocarbon monomers—which can be used as starting materials and intermediates—and toward conversion of these substances to suitable polymers.

The recent publication^{1,2,3} of methods for the synthesis of hexafluorobenzene (C_6F_6) in reasonable yields and quantities, has greatly accelerated progress in the field of completely fluorinated aromatic polymers. Hexafluorobenzene is an excellent starting material for the syntheses of some new monomers and polymeric compounds containing the perfluorophenyl or perfluorophenylene group. For the formation of polymer chains, derivatives of hexafluorobenzene that have at least two reactive functional groups are required. There are also structures contemplated in which the perfluorophenyl group is pendant (branch or side) to the polymer chains. For this purpose, monofunctional derivatives are also of great value. The uses of the two types of derivatives can be illustrated by consideration of two molecular structures, polyperfluorophenylene

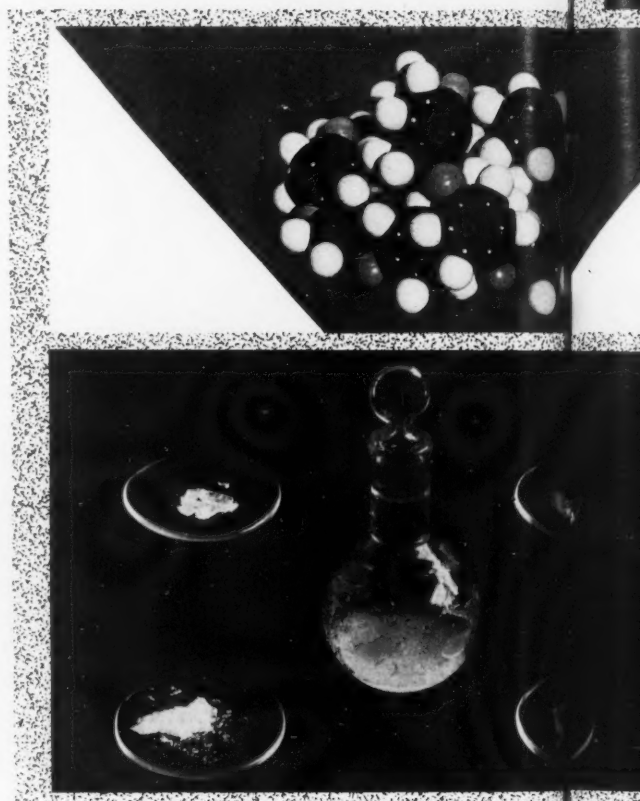


and poly(1,2,3,4,5-pentafluorostyrene)



The former, having a molecular weight of about 2,000, was prepared a few years ago from diiodotetrafluorobenzene while the monomer of the latter was recently produced from pentafluorobromobenzene.

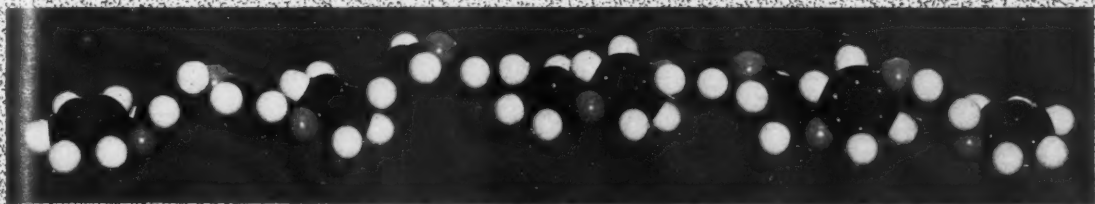
The stringent and often conflicting requirements for attaining a combination of high thermal stability and



plasticity (or rubberyness) in a material severely restricts the number of conceivable molecular structures. For example, linear flexible molecular chains, with a large number of configurational possibilities and strong chemical bonds between all the atoms in the molecule, are needed for the desired properties. A structure approaching this ideal is polyperfluorophenylene ether. Conversely, polyperfluorodiphenylsiloxane has a bulkier structure with considerable steric hindrance between the pendant pentafluorophenyl groups. It is evident that this polymer cannot be coiled without breaking bonds.

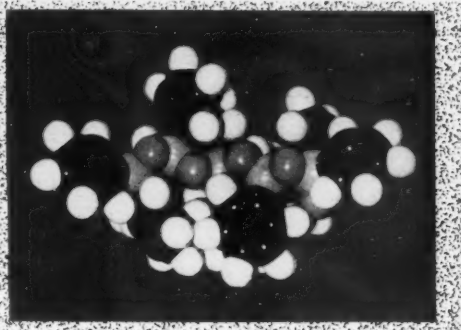
Hexafluorobenzene

The simplest and most direct method of synthesizing appreciable amounts of hexafluorobenzene involves heating tribromofluoromethane.¹ When the process is



Requirements for thermally stable, yet flexible, aromatic fluorocarbons include strong bonding between all the atoms and a long chain permitting existence in several configurations. For example, a high degree of flexibility is suggested by polyperfluorophenylene ether, shown in both an extended (above) and coiled (left) arrangement.

Five aromatic fluorocarbons (left) synthesized by the Bureau. Crystals are diiodotetrafluorobenzene (left foreground), tetrakis-pentafluorophenyl silane (right foreground), perfluorodiphenyl (left background), pentafluorobenzoic acid (right background); and the liquid (center) is pentafluorophenol.



The polyperfluorodiphenyl siloxane structure does not show a high degree of flexibility. The interfering pentafluorophenyl groups greatly hinder the number of possible configurations. The polymer could not be coiled without breaking bonds.

conducted in a platinum furnace at 540° C and at 50 to 265 psi pressure, yields of better than 55 percent have been obtained at the Bureau.²

A number of suitable intermediate compounds for making high-temperature polymers have been prepared from hexafluorobenzene. In one method, pyridine has

been selected as the solvent because it promotes certain nucleophilic (proton-seeking) reactions, especially with oxygen-containing bases.⁴ The addition of methanolic sodium hydroxide to the hexafluorobenzene-pyridine solution produces pentafluoroanisole,³ and the addition of solid potassium hydroxide to this same solution produces pentafluorophenol.⁴ When alcoholic potassium hydroxide is used as the base, pentafluorophenol, tetrafluorodihydroxybenzene, pentafluorophenetole, and a small amount of tetrafluorodiethoxybenzene are obtained. In liquid ammonia, pentafluoroaniline⁵ is produced from sodamide and benzene.

Hexafluorobenzene can be readily reduced by hydrogen with a platinum catalyst. The main products of this reduction, pentafluorobenzene and tetrafluorobenzene, can be brominated to pentafluorobromobenzene and dibromotetrafluorobenzene or iodinated to the analogous iodides. Since these compounds contain readily displaced atoms—bromine or iodine—in active sites, they can be used to prepare other aromatic fluorocarbons that cannot be directly synthesized from hexafluorobenzene. This is a step nearer the production of improved heat-resistant polymers.

Such reagents as methyl magnesium iodide can replace one or two of the fluorines in hexafluorobenzene to produce 1,2,3,4,5-pentafluorotoluene, or one or more of the possible tetrafluoroxylene. Since the hydrocarbon methyl group is easily oxidized to the carboxylic group, a relatively easy route to dicarboxylic tetrafluorobenzene, another polymer precursor, is obtained. Finally it should be noted that attempts to prepare such derivatives as sodium pentafluorophenyl have produced vigorous explosions.

Work on the radiolysis of hexafluorobenzene has shown that in the presence of high-energy radiation, the major products are larger molecules similar in nature and quantity to those found in benzene that has been irradiated. Thus aromatic fluorocarbons appear to have the same high order of radiation resistance as aromatic hydrocarbons. At high temperatures these fluorocarbon polymers, such as polyperfluorostyrene, may be expected to exceed the aromatic hydrocarbon polymers in radiation resistance.

Pentafluorobromobenzene and Its Grignard Reagent

The versatility of Grignard reagents (RMgBr) makes them suitable tools for synthesizing different

types of complex aromatic fluorocarbons. For example, the availability of the pentafluorophenylmagnesium bromide will permit the eventual synthesis of many different and complex aromatic fluorocarbons. Pentafluorobromobenzene, which is obtained as a by-product in the preparation of hexafluorobenzene by pyrolysis, can be readily converted to a Grignard reagent, which reacts with acetaldehyde to form pentafluorophenyl- α -ethanol. This resulting alcohol can be dehydrated at 350° C by alumina pellets to 1,2,3,4,5-pentafluorostyrene.

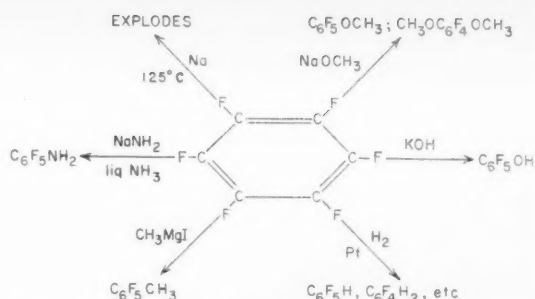
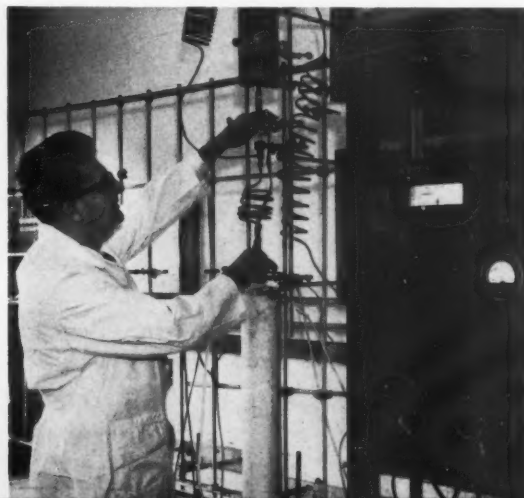
The preparation of perfluorostyrene, polymers of which are expected to exhibit good radiation resistance, is also an objective of the Bureau's work. At present, coupling reactions involving Grignard reagents have proven unsatisfactory; however, reactions with the pentafluorophenyl Grignard and tetrafluoroethylene are being explored. Reactions of the Grignard with various alkyl iodides lead to exchange and not to the desired coupling. With cobalt chloride, the pentafluorophenyl Grignard will react by coupling to form the perfluorodiphenyl.

A better synthesis of perfluorodiphenyl is by the Ullman condensation of pentafluorobromobenzene in a sealed tube at 250° C. With the silicon tetrachloride and phosphorous trichloride, the Grignard has been used to give the tetrakis-(pentafluorophenyl)-silane and tris-(pentafluorophenyl)-phosphine. Reaction with tin tetrachloride and boron trichloride should readily produce similar derivatives.

Condensation of Aromatic Amidines or Nitriles

It has been shown that aliphatic fluorinated compounds⁶ such as the perfluoroalkyl nitriles and dinitriles react with ammonia to form perfluoroalkylamidines or diamidines, and these condense to form polymers. An analogous reaction with aromatic substances would be pentafluorobenzonitrile (recently synthesized at the Bureau) and perfluorophthalyl dinitrile forming, respectively, pentafluorobenzamidine and perfluorophthalyl diamidine. Since the aliphatic polymeric ami-

Scientist adjusts equipment for synthesis of hexafluorobenzene. Synthesis involves pyrolysis of tribromofluoromethane at 50 to 265 psi pressure.



Some of the compounds prepared from C_6F_6 . Because numerous types of intermediate compounds can be formed from hexafluorobenzene, it is used as a versatile starting material in the synthesis of aromatic fluorocarbon polymers.

dines are bonded through the triazine structure, corresponding polymeric structures resulting from the aromatic amidines—and consequently incorporating the triazine—would have additional stabilizing resonance energy. This energy, created by the conjugated (i.e., having alternate double and single bonds) completely cyclic structure, would provide the amidine with greatly improved thermal stability. Then, too, the material would possess excellent rubber-like properties over a wide range of temperature due to the numerous possible configurations in which such a structure may exist. Combinations of an aromatic and an aliphatic perfluoroamidine may produce copolymers with other improved properties.

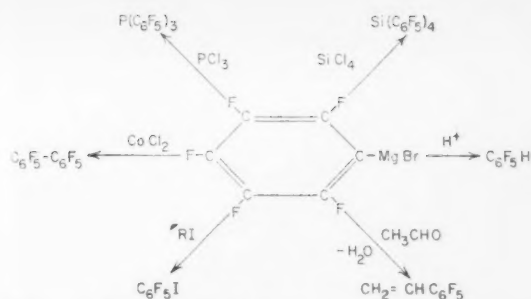
Perfluoroaromatic Ethers

Sodium and silver pentafluorophenolates were prepared from pentafluorophenol. When the sodium derivative was thermally decomposed in a vacuum, the main products were an alkali-insoluble solid and a brown tacky gum. The white solid, when pure, melted between 163° and 165° C and is believed to be the ortho dimer of pentafluorophenolate, while the gum is believed to be a low-molecular-weight polyether derivative. Research is being continued to increase the molecular weight of this polymer.

Efforts to prepare the perfluorodiphenyl ether from the sodium pentafluoroether and hexafluorobenzene have been unsuccessful. Apparently the pentafluorophenol is a strong acid, and since its sodium salt is a neutral compound, the reaction mixture is not sufficiently basic to attract fluorine from a hexafluorobenzene ring. However, a small yield was obtained from the silver salt and hexafluorobenzene.

Although attempts to pyrolyze the silver salt in a sealed tube at 200° C resulted in an explosive reaction, this same silver compound could be heated for several hours without detonation when a trace of iodine was added. It is possible that the iodine inhibits the formation or decomposition of perfluorodiphenyl peroxide which might decompose explosively on heating.

Unlike the sodium salts, the silver salts have the added property of photochemical decomposition and



Compounds synthesized from the Grignard reagent ($\text{C}_6\text{F}_5\text{MgBr}$). Derivatives of this substance are excellent intermediates in the preparation of potential high-temperature-resistant fluorocarbon polymers.

may react to form polymers that it is not possible to obtain with the sodium derivatives. A polymeric glassy substance was obtained from silver pentafluorophenolate and trifluoroiodoethane after illumination with a 250-watt photo flood light for 6 hr. As yet, it is not certain whether this product is a polyperfluoroethylene, a polymer of perfluorophenoxytetrafluoroethylene, or some iodine compound.

When the silver salt was pyrolyzed or decomposed by illumination, none of the dimeric products that were obtained with the sodium derivatives were observed. This result is probably due to steric inhibition caused by the large silver molecule.

Numerous other fluorinated aromatic compounds are being studied. Each of the new materials synthesized is capable of further reactions to produce still more perfluoroaromatic monomers and related compounds.



To avoid contact with moisture in the atmosphere, scientist conducts reactions involving an anhydrous fluorocarbon Grignard reagent in a dry box.

¹Y. Desirant, *Bul. Acad. Roy. Belg. Classe Sci.* [5] **41**, 759 (1955).

²Hexafluorobenzene from the pyrolysis of tribromofluoromethane, M. Hellman, E. Peters, W. J. Pummer, and L. A. Wall, *J. Am. Chem. Soc.* **79**, 5654 (1957).

³J. A. Godsell, M. Stacey, and J. C. Tatlow, *Nature* **178**, 199 (1956).

⁴Reactions of hexafluorobenzene, W. J. Pummer and L. A. Wall, *Science* **127**, 643 (1958).

⁵E. J. Forbes, R. D. Richardson and J. C. Tatlow, *Chem. & Ind.* 630 (1958).

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Determination of Dielectric Constants of Pure Liquids

AS PART of a Bureau program to obtain more precise information on the dielectric properties of scientifically and industrially important pure liquids, the dielectric constant of deuterium oxide (heavy water)¹ has been determined with a high degree of accuracy. Although the a-c bridge method used in this determination is not basically new, it incorporates several techniques and procedures, developed by C. G. Malmberg and A. A. Maryott, which extend the range and accuracy of the method, particularly when dealing with semi-conducting liquids.

Evaluation of the results obtained with deuterium oxide and other liquids indicates that with suitable cells this method is generally useful for accurate measurements of the dielectric constant of liquids whose conductivity may range as high as 5 micromho/cm. For liquids of low conductivity (10^{-3} micromho/cm or less) an accuracy in dielectric constant approaching 0.01

percent may be possible. This method is simultaneously useful for adequate determinations of conductivity down to 10^{-5} micromho/cm.

Determinations of the dielectric constant of deuterium oxide were conducted at 5-deg intervals between 4° and 100° C. These and corresponding values for ordinary water² were made at conductivities up to nearly 2 micromho/cm. Samples of heavy water containing 99.4-mole percent deuterium oxide were used to obtain precise data from which static values of the dielectric constant (ϵ) of deuterium oxide were derived. The data were reproducible to better than ± 0.01 unit and the values are believed to be accurate to ± 0.05 units or better. The temperature coefficient [the fractional change of dielectric constant with temperature, $(1/\epsilon)(d\epsilon/dt)$] varies by less than 1.5 percent between 4° and 100° C while the uncertainty in the measured values of this coefficient is believed to be less than 1 part in 100.

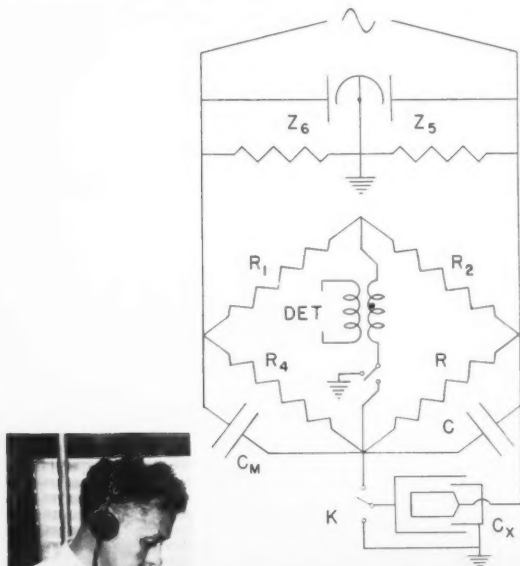
A general survey of the literature on pure liquids³ has shown that the dielectric constants of only a few liquids are known to better than ± 0.2 percent. In the usual case, the uncertainty is of the order of 1 or 2 percent. The temperature dependence is, in general, correspondingly less well known—if at all. Considering the sources of error involved, the discrepancies observed in the literature are probably the result of some combination of imperfections in the procedures employed and of impurity of the sample.

Since the dielectric constant is a measure of the "displacements" that the electric charges inside a medium undergo when acted on by an electric field, a knowledge of the dielectric properties of a material can lead to understanding of its molecular structure and its physical and chemical behavior. Data on dielectric constants help the physical chemist, in particular, to interpret various properties of solutions and to understand solvent effects as they influence reaction rates and equilibrium constants. Furthermore, a knowledge of the properties of heavy water is important in nuclear research.

The Dielectric Constant

The fundamental principle involved in the measurement of dielectric constants is that for a given charge, the field strength between the plates of a capacitor is inversely proportional to its capacitance—which is

Schematic diagram (left, above) of a bridge circuit and Wagner earth used for dielectric constant determinations. The a-c source is at the top, Z_5 and Z_6 designate the Wagner earth. In the bridge proper, R_1 and R_2 represent the equal ratio arms; R_4 and C_M , the variable standard resistance and capacitance; R and C , the fixed ("zero" balance) resistance and capacitance; and C_X , the test cell. Left: Scientist balances the bridge with a cell mounted in the thermostat in foreground. Bridge network must be balanced to obtain data in the determination of dielectric properties of material.



itself directly proportional to the dielectric constant of the medium between the plates. Practical determinations on liquids are commonly made by measurement of the relative capacitance of a test capacitor with air (or some other standard), and with the material under study between the plates. The dielectric constant, ϵ_x , of the material is then given by

$$\epsilon_x = \epsilon_0 (C_x / C_0),$$

where ϵ_0 is the dielectric constant of air and C_x and C_0 are the capacitances for the material and air, respectively.

The cells used for liquids are usually of the type with a fixed replaceable capacity. For "absolute" determinations, suitable bridge techniques with three-terminal cells can be used to advantage in obtaining linear correspondence of the measured capacity and dielectric constant.

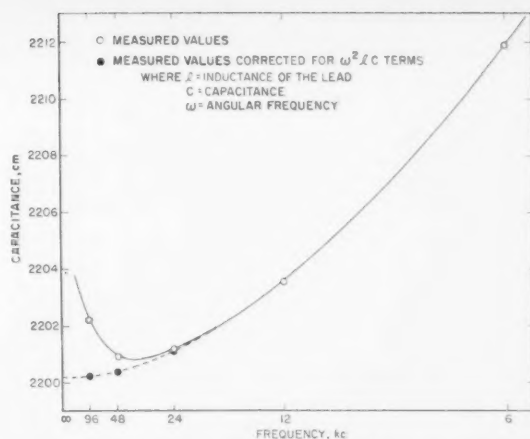
From a study of sources of error involved in measurements on liquids by bridge methods, certain procedures and techniques were evolved to minimize the influence of these sources and to evaluate the required corrections. Among the factors considered were improvement in cell design, evaluation of frequency-dependent and conductance-dependent errors, and specialized purification of the liquid as required.

Checks made on the stability of the system were satisfactory in that they showed it to be stable within the precision achieved.

Apparatus

The test cell in these experiments, constructed of copper with tin surfaces and glass-teflon insulation, is a fixed 3-terminal capacitor of cylindrical shape. It is designed for stability, minimum temperature coefficient, and maximum useful working capacity. The central high-potential electrode in the cell is supported by the guard electrode which, in turn, is enclosed in the guarded electrode generally maintained at earth potential. This arrangement differs somewhat from the more usual design in which the grounded electrode surrounds the guarded electrode and acts as a shield for the cell. With the present cell, less insulation is required, making construction simpler and more compact, and reducing the electrode-to-guard admittances.

A capacitance-conductance bridge network² provided with a Wagner earth is used to measure the cell capacitance. The electrical source is a tuned-circuit oscillator variable from 30 cps to 200 kc and the detector is an audio amplifier or a regenerative receiver with headphones. The ratio arms of the bridge are equal 1,000-ohm resistors and the balancing arm contains the standards—a precision variable capacitor in parallel with a high-quality variable a-c resistor. The "unknown" arm contains a resistor and capacitor in parallel. By suitable switching, the working capacity of the test cell can be connected in parallel with the "unknown" arm or with a branch of the Wagner earth to establish a "zero" balance of the bridge. The difference between these balances, as measured on the standard capacitor, is free of error due to the insulation and lead capacity of the cell. When corrected



Typical curve showing the influence of frequency-dependent error. Error caused by electrode polarization may be eliminated by use of a graph showing measured capacity plotted against the reciprocal of the frequency of measurement. When the graph is corrected for frequency-dependent lead-inductance error, the error due to electrode polarization can be eliminated by short-range extrapolation to infinite frequency.

for the influence of other sources of effective capacitance, it is proportional to the dielectric constant of the medium in the cell.

Reduction of Conductivity

Since the errors dependent on conductivity are roughly proportional to its square, a low conductivity is required. In the case of the heavy water samples, the main impurity was found to be ordinary water. This is not particularly objectionable in so small a quantity—0.6 mole percent—especially since the dielectric constants of water (H_2O) and deuterium oxide (D_2O) are very similar. Of much greater consequence as a source of error was the presence of minute amounts of ionizable impurity which raise the conductivity of the liquid.

Objectionable impurities in the sample of heavy water were eliminated by using a two-stage still. Volatile acidic and basic impurities were retained in the still's evaporators by chemical means. By recirculating the purified distillate through the test cell, contamination by the cell itself was reduced and the conductivity brought within the desirable limits.

Minimization of Errors

Selection of the bridge network used was influenced primarily by the degree to which sources of error could be eliminated and the corrections for the remaining error evaluated. Balance of the capacitance-conductance network is basically independent of frequency. Since effects of electrode phenomena and of unbalanced lead inductance show frequency dependence, their presence is evident and subject to evaluation from measurements made over a wide range of

Dielectric constant and temperature coefficient values for ordinary and heavy water

These data are considered accurate to ± 0.05 unit

Temperature	ϵ		$(1/\epsilon)(d\epsilon/dt)$	
	D ₂ O	H ₂ O	D ₂ O	H ₂ O
° C				
4	85.88	86.15	4.63×10^{-3}	4.56×10^{-3}
15	81.62	81.95	4.62	4.55
25	77.94	78.30	4.61	4.54
50	69.47	69.91	4.59	4.53
75	61.96	62.43	4.57	4.53
100	55.28	55.72	4.56	4.57

frequency. Because its "zero" balance is practically independent of frequency, a comparative method for use of the bridge here shows a distinct advantage over the alternate substitution method. As a result, the magnitude of the frequency-dependent error becomes readily evident and may be evaluated by a semi-graphic procedure.

The errors that depend primarily upon the resistance balance are less evident but no less serious in their effect. They are associated with the various lead in-

ductances, variations of reactance of the resistance standard, and any inequality of reactance of the ratio arms. The required corrections for these errors were determined by using a procedure which was essentially equivalent to measuring all capacities at zero conductivity.

With semiconducting liquids such as deuterium oxide, sufficient stability of cell resistance to obtain precise capacitance balance is often difficult to maintain. This may be due to various electrode phenomena and to contamination of the medium by the atmosphere or the cell material. When instability is unusually high, operation at higher frequency is indicated because the bridge balance becomes more sensitive to changes in capacity and less sensitive to the resistance at increasing frequencies.

¹ For further information, see Dielectric constant of deuterium oxide, C. G. Malmberg, *J. Research NBS* **60**, 609 (1958) RP2874.

² Dielectric constant of water from 0° to 100° C, C. G. Malmberg and A. A. Maryott, *J. Research NBS* **56**, 1 (1956) RP2641.

³ A. A. Maryott and E. R. Smith, Table of dielectric constants of pure liquids, *NBS Circ.* 514 (1951).

Bonding of Gold to Fused Silica

TO PROVIDE basic information on the mechanism of ceramic-metal bonding, the bonding of gold to fused silica has been investigated at the Bureau of work partially supported by the Navy Bureau of Aeronautics.¹ A clearer understanding of the bonding mechanism should be useful in obtaining stronger bonds between ceramics and metals.

Ceramic-metal bonding includes such processes as glass-metal sealing, porcelain enameling, and the ceramic coating of alloy parts. The sealing of glass to metal has been an important process for many years in manufacturing incandescent lamps. Similar glass-metal seals have been used for radio and television tubes, fluorescent lamps, and some types of particle accelerators. Porcelain enameling, which provides a decorative, as well as a protective, finish to such household items as sinks, stoves, and bathtubs, depends on strong bonds for its successful use. Also the ceramic coating of metals and alloys to resist corrosion and oxidation at high temperatures, hinges on the formation of a strong bond between the metal and the ceramic.

In general, bonding theory has not kept pace with industrial applications. Even though numerous theories have been advanced to explain the mechanism of bonding, none have been widely accepted. The studies on gold-silica bonding, recently conducted by D. G. Moore and H. R. Thornton of the NBS staff, should prove useful in resolving some of these theories.

The test specimens were prepared by melting gold pellets in vacuum on plaques of polished fused silica and then heating for 15 min at 1,100° C under various oxygen and air pressures. The effects of oxygen and air pressure, gold diffusion into the silica lattice, gas evolution, and surface roughening were analyzed to determine their significance to the bonding mechanism.

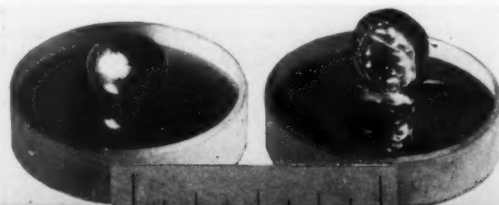
Bond strength was measured at room temperature with a shear testing apparatus. Examinations with a polarograph showed the silica to be substantially free of strain prior to testing.

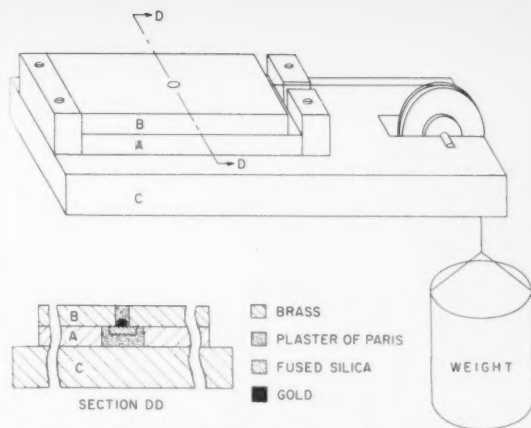
Gold diffusion was studied by a technique in which the radioactive isotope of gold, Au¹⁹⁸, was used as a tracer. After the gold pellet was removed from the silica plaque with aqua regia, the residual radioactivity indicated that gold had diffused into the silica lattice at relatively high oxygen and air pressures but not during vacuum heating.

Although gold oxides are known to be unstable above 250° C, the bonding and diffusion, which occurred only in the presence of oxygen and air suggests that molten gold will combine with oxygen under some conditions. When a relatively small amount of the gold oxide diffuses into the silica lattice, a strong chemical bond appears to develop between the metallic gold and the gold-enriched layer of silica. Thus, a probable explanation for the adhesion is the formation of a chemical bond between the metal and the ceramic.

One bonding theory suggests that the ceramic becomes mechanically locked to the metal by the formation of "anchor points" at the interface. Electron-micrographs, however, showed only a very slight etching or pitting for the specimens treated in oxygen. Such an effect is insufficient to provide a strong mechanical gripping between the metal and ceramic.

Gold pellets used in studies on ceramic-metal bonding are melted on ½-in. diam. fused-silica plaques.



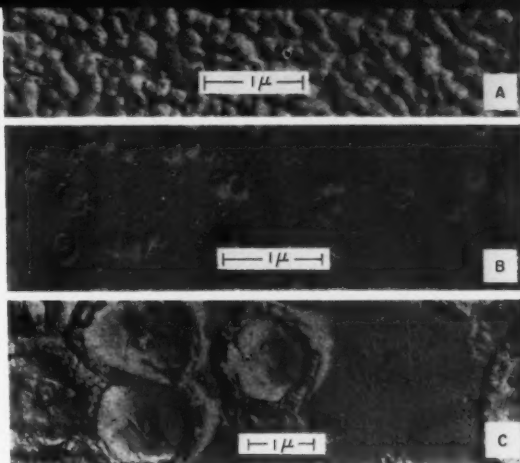


Schematic diagram of the shear test apparatus used to determine the bond strength between a gold pellet and a silica plaque. At room temperature, the shearing force varied from zero for pellets in a vacuum to 640 and 725 psi for those heated in air and oxygen, respectively.

Thus, mechanical interlock can be practically eliminated as a possible mechanism for the bonding.

All specimens except those tested in vacuum showed gas occlusions present at the interface. Although the composition of the gas was not determined, it is probably oxygen.

A thermodynamic approach to bonding predicts a relationship between contact angle, which is a measure of wetting or spreading, and bond strength. However, no such relationship was found for specimens treated in oxygen and vacuum. The contact angles were 136° in oxygen and 138° in vacuum, but the shear strengths



Electron micrographs are used to study the fused silica surface from which gold pellets have been removed with aqua regia. (A) Typical appearance near the outer edge of the contact area; (B) area of lesser attack; and (C) peculiar craterlike attack at one location near the gold-silica-oxygen interface.

were 640 psi and zero, respectively.

Data from an additional experiment suggested that the contact angle in air is dependent on the lateral diffusion of gold oxide and that the angles measured after only 15 min of heating are not true equilibrium angles. Prolonged heating of specimens to test this hypothesis was not practical because of crystallization of the fused silica.

¹ For further technical details, see Effect of oxygen on the bonding of gold to fused silica, by D. G. Moore and H. R. Thornton, *J. Research NBS* 62, 107 (1959) RP2942.



SCRIBNER RECEIVES SPECTROSCOPY AWARD

BOURDON F. SCRIBNER, Chief of the Spectrochemistry Section and Acting Chief of the Spectroscopy Section, has received the 1959 award of the Spectroscopy Society of Pittsburgh. Mr. Scribner was cited for "outstanding contributions to the science of spectroscopy." The award, consisting of a plaque and \$300, was presented at the Society's meeting on March 5, 1959.

Born April 13, 1910, in Westernport, Maryland, Mr. Scribner joined the Bureau in 1927, where he served for many years in the Spectroscopy Section. He received his B.S. degree in chemistry from George Washington University in 1933, and his

M.S. degree in physical chemistry from the University of Maryland in 1939. From 1942 to 1947, he supervised a group under the Manhattan Project, developing and applying spectrochemical methods to the analysis of uranium and related materials. In 1947 he was appointed chief of the Bureau's newly formed Spectrochemistry Section, which has the responsibility for research and testing in spectrochemical analysis and for the preparation of standard samples for calibration in this field.

Mr. Scribner is a member of the American Chemical Society's panel on the Advances in Chemistry Series. He has held several offices in the Washington Section, ACS, and served as editor of *The Capital Chemist* for several years. He has also served on the Emission Spectroscopy Committee of the American Society for Testing Materials, and received the Society's Award of Merit in 1958. He received the Department of Commerce Meritorious Service award in 1948.

Mr. Scribner is also on the editorial board of *Spectrochimica Acta*, and is a member of the Washington Academy of Sciences, the Instrument Society of America, and the Optical Society of America. He is the author of over 40 publications in basic and applied spectroscopy.

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U.S. DEPARTMENT OF COMMERCE

LEWIS L. STRAUSS, *Secretary*

NATIONAL BUREAU OF STANDARDS

A. V. ASTIN, *Director*

April 1959 Issued Monthly Vol. 43, No. 4

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Publications of the National Bureau of Standards

Periodicals

Journal of Research of the National Bureau of Standards, Volume 62, No. 3, March 1959 (RP2935 to RP2942 incl.) 60 cents.

Technical News Bulletin, Volume 43, No. 3, March 1959. 15 cents. Annual subscription \$1.50, 75 cents additional for foreign mailing.

Basic Radio Propagation Predictions for June 1959. Three months in advance. CRPL-D175. Issued March 1959. 10 cents. Annual subscription \$1.00, 50 cents additional for foreign mailing.

Research Papers

Journal of Research, Volume 62, No. 3, March 1959. 60 cents.

RP2935. On a theorem of M. Riesz. Martin Pearl.

RP2936. Refinement of the crystal structure of triclinic magnesium pyroborate. Stanley Block, Gordon Burley, Alvin Perloff, and Robert D. Mason, Jr.

RP2937. Heat transfer in laminar flow through a tube. Milton Abramowitz, William F. Cahill, and Clarence Wade, Jr.

RP2938. Fluorination of haloaromatic compounds. Roland E. Florin, Walter J. Pummer, and Leo A. Wall.

RP2939. Synthesis of some disubstituted 3,4,5,6-tetrafluorobenzenes. Walter J. Pummer, Roland E. Florin, and Leo A. Wall.

RP2940. Reactions of aromatic fluorocarbons with hydrogen. Roland E. Florin, Walter J. Pummer, and Leo A. Wall.

RP2941. Exponential integral $\int_1^x e^{-zt} t^{-n} dt$
for large values of n . Walter Gautschi.

RP2942. Effect of oxygen on the bonding of gold to fused silica. D. G. Moore and H. R. Thornton.

Circulars

C597. Energy spectrum resulting from electron slowing down. Rosemary T. McGinnies. 20 cents.

Building Materials and Structures Reports

BMS140 (3d Edition). Selected bibliography on building construction and maintenance. Edith R. Meggers. 30 cents.

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Recent theoretical studies of the propagation of long waves. J. R. Wait. (Abstract) *Congres International sur la Propagation des Ondes Radi-Electriques*, Liege (6-11 Octobre 1958).

An on-off temperature control for electrically heated filaments. Roger E. Little and John D. McKinley, Jr. *Rev. Sci. Instr.* 29, No. 12, 1143 (1958).

A method for measuring the directivity of directional couplers. G. E. Schafer and R. W. Beatty. *I.R.E. Trans. on Microwave Theory Tech.* MTT-6, No. 4 (1958).

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Mechanisms of polymer formation and decomposition. Robert Simha and Leo A. Wall. Chapter in book, *Catalysis* 6, p. 191 (Reinhold Publishing Corp., New York, N.Y., 1958).

Publications for which a price is indicated are available only from the Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. (foreign postage, one-fourth additional). The Technical News Bulletin and Basic Radio Propagation Predictions are available on a 1-, 2-, or 3-year subscription basis, although no reduction in rates can be made. Reprints from outside journals and the NBS Journal of Research may often be obtained directly from the authors.

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